THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Three-Leaf Quantum Interference Clovers in a Trigonal Single-Molecule Magnet

Citation for published version:

Atkinson, JH, Inglis, R, del Barco, E & Brechin, EK 2014, 'Three-Leaf Quantum Interference Clovers in a Trigonal Single-Molecule Magnet', *Physical Review Letters*, vol. 113, no. 8, 087201.
<https://doi.org/10.1103/PhysRevLett.113.087201>

Digital Object Identifier (DOI):

[10.1103/PhysRevLett.113.087201](https://doi.org/10.1103/PhysRevLett.113.087201)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Physical Review Letters

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Three-Leaf Quantum Interference Clovers in a Trigonal Single-Molecule Magnet

James H. Atkinson,¹ Ross Inglis,² Enrique del Barco,^{1,*} and Euan K. Brechin²

¹*Department of Physics, University of Central Florida, Orlando, Florida 32765, USA*

²*EaStCHEM School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom*

(Received 7 May 2014)

1 We report on a single-molecule magnet where the spatial arrangement of three manganese ions and their spin-orbit coupling tensor orientations result in threefold angular modulations of the magnetization tunneling rates and quantum interference patterns that mimic the form of a three-leaf clover. Although expected in all quantum tunneling of magnetization resonances for a trigonal molecular symmetry, the threefold modulation only appears at resonances for which a longitudinal magnetic field is applied (i.e., resonance numbers $|k| > 0$). A sixfold transverse field modulation observed at a resonance of $k = 0$ manifests as a direct consequence of a threefold corrugation of the spin-orbit coupling energy landscape, creating an effective longitudinal field which varies the resonance condition in the presence of a transverse field. The observations allow for an association between the trigonal distortion of the local spin-orbit interactions and the spatial disposition of the constituent ions, a finding that can be extrapolated to other systems where spin-orbit coupling plays a significant role.

DOI:

PACS numbers: 75.50.Xx, 03.65.Vf, 75.45.+j

4 One of the most prominent findings since the discovery of single-molecule magnets (SMMs) [1,2] is the significance of Berry phase interference (BPI) as a modulator of quantum tunneling of magnetization (QTM) [4–6], which established the importance of the subtle contributions of spin-orbit interactions in QTM behavior. It is in the kernel of this understanding where one finds insight into the relationship between the spin-orbit coupling (SOC) symmetries and QTM, including the symmetry-imposed spin selection rules. These rules state that in order for tunneling to occur between two spin eigenstates, labeled as m and m' , at a QTM resonance $k = mn - m$, k must be an integer multiple of the lower molecular symmetry. As such, in molecules of rhombic symmetry, only resonances corresponding to a multiple of two are unfrozen, while trigonal and tetragonal symmetries only lift state degeneracies at resonances $k = 3 \times n$ and $k = 4 \times n$ ($n = \text{integer}$), respectively. These apparently clear restrictions have puzzled researchers in the field for two decades, as evidence for tunneling has been observed at all QTM resonances for most SMMs regardless of their respective molecular symmetry. The only exception so far has been a Mn₃ SMM of trigonal symmetry [13], in which the absence of a resonance ($k = 1$) provided the first clear evidence of spin selection rules. However, the appearance of other resonances also forbidden by symmetry (i.e., $k = 2$) in that molecule and the inability to study the detailed field dependence of the different tunnel splittings have dimmed the relevance of that finding, since its interpretation has relied exclusively upon theoretical analyses derived from indirect results (see Refs. [14–16]).

The lowest symmetry that supports QTM in odd-numbered resonances is trigonal. This is an important case

study, as only a transverse magnetic field can break the degeneracy between the spin levels at odd-numbered resonances. It is worth noting that internal fields (e.g., dipolar or nuclear) are not sufficiently large enough to explain the observed tunneling rates in forbidden resonances. Thus far, the only indirect evidence of a trigonal molecular symmetry has been a sixfold magnetic field angular modulation of the electron paramagnetic resonance spectra in a heteronuclear Fe₃Cr SMM [16], while the corresponding modulation of the QTM remains unobserved for this symmetry. It is in this Letter where the first manifestation of a threefold modulation of the QTM rates in a SMM is presented. We also detail a number of related fascinating behaviors, including the first observation of a spatial corrugation of the intrinsic SOC energy landscape. The results presented here represent an important step forward in the effort to reconcile the theory of QTM with observation, and shed light on the answers of many long-standing questions.

The SMM complex we studied has the formula Mn₃O(Et – sao)₃(Et – py)₃ClO₄ (henceforth referred to as Mn₃). Chemical analysis [17] ascribes the magnetic behavior to a core containing three Mn^{III} ions ($s = 2$) ferromagnetically coupled via a superexchange interaction, resulting in an $S = 6$ ground state. A schematic constructed from x-ray diffraction measurements is inset in Fig. 1 (see Ref. [17] for more details).

Figure 1 shows magnetization hysteresis loops obtained from a crystalline sample of Mn₃ SMMs with a field applied along the easy anisotropy axis (z axis) at different temperatures. Note that resonance $k = 1$ does not appear below 1.35 K, due to the selection rules discussed above which forbid this resonance under trigonal symmetry

FIG. 1 (color online). Stepwise magnetic hysteresis loops characteristic of resonant QTM obtained in a single crystal of $\text{Mn}_3\text{O}(\text{Et}-\text{sao})_3(\text{Et}-\text{py})_3\text{ClO}_4$ SMMs at different temperatures. Up to six resonances can be observed ($k = 0, \pm 1, \pm 2, \pm 3, \pm 4$, and ± 5), including steps associated with QTM through excited states ($k = 1e, 2e, 3e, n$). The inset shows the Mn_3 core.

considerations (i.e., $k \neq 3 \times n$). The QTM spectroscopy (i.e., position of the resonances) in this figure allows for determination of the spin Hamiltonian governing the sample's quantum dynamics. In the giant spin approximation (GSA), the molecule is considered as a single rigid spin (S) modeled by an interaction Hamiltonian, by which a trigonal symmetry can be written as follows:

$$\hat{H}_{\text{GSA}} = D\hat{S}_z^2 + B\hat{S}_z^4 + B_4^3O_4^3 + B_6^6O_6^6 + \mu_B \mathbf{B} \cdot \vec{g} \cdot \hat{\mathbf{S}}. \quad (1)$$

The first four terms characterize the zero-field splitting anisotropy, with the first usually dominant and responsible for the easy magnetization axis of the molecule (with a quartic axial correction given by the second). The Stevens spin operators (O_p^q) are restricted by the spin value ($p \leq 2S$) and the rotational symmetry, $q(\leq p)$. Here we consider only second- ($\hat{S}_z^2 = O_2^0$, with $D = 3B_2^0$) and fourth-order ($B\hat{S}_z^4$) axial terms and the leading trigonal ($O_4^3 = \frac{1}{2}[\hat{S}_z, \hat{S}_+^3 + \hat{S}_-^3]$) and hexagonal ($O_6^6 = \frac{1}{2}[\hat{S}_+^6 + \hat{S}_-^6]$) transverse operators. The final term is the spin-field Zeeman interaction. The QTM behavior in Fig. 1 can be well explained by diagonalization of the GSA Hamiltonian assuming an isotropic $g = 2$, $D = -0.86$ K, and $B = 1.4$ mK (the transverse anisotropy terms have a negligible effect on the spin projection energies, being only significant at degeneracies). Figure S1 in the Supplemental Material [19] shows the correspondence between the QTM spectroscopy data and the levels of the $S = 6$ spin multiplet.

We will focus the following discussion on the behavior of the QTM resonances as a function of both the angle and magnitude of the transverse field, H_T (see also Fig. S2 in the Supplemental Material [19] for a visualization of the molecular axes as defined by the molecular anisotropy). We define the QTM probability P_k as the normalized change in magnetization that occurs as the longitudinal field H_L is

swept through a resonance. This probability is related to the “tunnel splitting” Δ_k (which breaks the degeneracy between opposite spin projections) by the Landau-Zener formula [18], $P_k = 1 - \exp[-\pi\Delta_k^2 n / 2\nu_0\delta]$, where $\nu_0 = g\mu_B(2S - k)$, δ is the field sweep rate and n is the number of times resonance k is crossed. To extract the angular dependence of P_k , a fixed transverse field is maintained at a given angle ϕ within the molecular xy plane while the longitudinal field is swept across the resonance under study. The process is then repeated for different ϕ ranging from 0° to 360° . In order to optimize the quality of the results, and overcome several technical limitations, different protocols of measurement were followed for each resonance, as explained in Sec. 2 of the Supplemental Material [19].

Let us focus first on resonance $k = 0$. Figure 2(a) shows a polar plot of $P_{k=0}$ vs ϕ , where an extraordinary sixfold modulation emerges, with sharp minima occurring at angles $\phi_{\text{min},k=0}^{\text{BPI}} = 32.6^\circ + m \times 60^\circ$ which correspond to BPI tunnel quenching. However, this sixfold appearance can be misleading; the expected symmetry of the molecule is threefold, and so the shape of the resonance behavior should be as well (in fact, we observe such modulation in all the other resonances, as discussed below). Within the GSA, this anomaly is a consequence of the trigonal transverse SOC anisotropy term, $O_4^3 = [\hat{S}_z, \hat{S}_+^3 \pm \hat{S}_-^3]$,

FIG. 2 (color online). (a) Sixfold modulation of the QTM probability in resonance $k = 0$ as a function of the angle of a 1.05 T transverse field in the molecular xy plane. Sharp minima appear every 60° . (b) Illustration of the threefold corrugation of the hard anisotropy plane which defines the longitudinal compensating field. (c) Data from our compensating field measurement (circles). The continuous line represents the fitting from diagonalization of the MS Hamiltonian in Eq. (2). (d) Threefold modulation of the QTM probability in resonances $k = \pm 1$ as a function of the angle of a 0.65 T transverse field within the molecular xy plane, with sharp minima appearing every 120° .

144 **8** which commutes the axial ($\hat{S}_z$) and the third-order creation
 145 or annihilation ($\hat{S}_+^3 \pm \hat{S}_-^3$) spin operators. Apart from
 146 generating a threefold modulation of the anisotropy barrier
 147 [see Fig. S2(b) in the Supplemental Material [19]], this
 148 term acts as an effective longitudinal field and produces a
 149 threefold corrugation of the hard anisotropy plane in the
 150 presence of transverse field, as illustrated in Fig. 2(b), and
 151 requires an offsetting or “compensating” longitudinal field
 152 (h_L) in order to bring the system back into resonance. This
 153 effect is extremely subtle and difficult to observe for the
 154 ground state splitting at resonance $k = 0$ (which mixes
 155 states $m = +6$ and $m' = -6$) in the range of H_T explored
 156 in these experiments, since the magnitude of h_L (< 3 G) is
 157 much smaller than the effective field width of the resonance
 158 (~ 2000 G at $H_T = 1.2$ T). As explained in Sec. 2 of the
 159 Supplemental Material [19], a sophisticated measurement
 160 protocol was employed in order to discern the contribution
 161 of the compensating field, with measurements performed
 162 at higher temperature ($T = 1.57$ K) for which the $k = 0$
 163 tunneling occurs predominantly through the third excited
 164 tunnel splitting (mixing states $m = +3$ and $m' = -3$). The
 165 corrugation is much more pronounced in this splitting
 166 as a result of its commensuration ($\Delta m = 3 \times n$) with the
 167 symmetry of the trigonal SOC term. The results are
 168 displayed in Fig. 2(c), where the compensating field shows
 169 an alternation between -55 and $+55$ Gauss with an overall
 170 threefold oscillation pattern. Interestingly, its absolute
 171 maximum values, found at $\varphi_{\max}^{h_L} = 50^\circ + n \times 60^\circ$, do not
 172 coincide with the angular positions of the BPI minima in
 173 this resonance ($\varphi_{\min, k=0}^{\text{BPI}} = 32.6^\circ + n \times 60^\circ$), as would have
 174 been expected from Eq. (1).

175 The trigonal symmetry of this SMM becomes obvious
 176 in the resonances that require a nonzero longitudinal field,
 177 i.e., $|k| > 0$, and which produce clear threefold angular
 178 modulations of the QTM probabilities. Data for $k = \pm 1$ are
 179 shown in Fig. 2(d) (see Fig. S4 of the Supplemental
 180 Material [19] for $|k| > 1$). For positive longitudinal fields
 181 (solid black circles) minima are found at $\varphi_{\min, k>0}^{\text{BPI}} =$
 182 $107^\circ + n \times 120^\circ$, and correspond to conditions for destruc-
 183 tive BPI. As a fascinating consequence of this symmetry,
 184 the anisotropy axes are “hard” and “medium” simultane-
 185 ously, depending on the direction of both the longitudinal
 186 and transverse applied fields. If the longitudinal field is
 187 reversed, as in resonances $k < 0$ [open red circles in
 188 Figs. 2(d) and Fig. S4 [19]], the threefold modulation is
 189 shifted by 60° , with minima appearing at $\varphi_{\min, k<0}^{\text{BPI}} =$
 190 $47^\circ + n \times 120^\circ$, a consequence of the time-reversal invari-
 191 ance upon full reversal of the total magnetic field.

192 We now turn our attention to the modulation of the QTM
 193 as a function of the magnitude of the transverse magnetic
 194 field applied along the “hard-medium” axes within the
 195 molecular xy plane, i.e., $\varphi_{\min, k=0}^{\text{BPI}} = 32.6^\circ (+180^\circ)$ for $k = 0$
 196 and $\varphi_{\min, |k|>0}^{\text{BPI}} = 107^\circ (+180^\circ)$ for $k > 0$. The results are
 197 shown in Fig. 3: $k = 0$ (solid black circles), $k > 0$ (solid
 198 red, green, and blue data points), and $k < 0$ (open data

points). BPI minima are found near $H_{T, k=0}^{\text{BPI}} = \pm 1.05$ T,
 $H_{T, k=\pm 1}^{\text{BPI}} = \pm 0.57$ T, $H_{T, k=\pm 2}^{\text{BPI}} = \pm 0.50$ T, and $H_{T, k=\pm 3}^{\text{BPI}} =$
 ± 0.35 T (marked by arrows). These are the same trans-
 verse fields chosen for the angular modulation measure-
 ments in Figs. 2 and S4 (with the exception of $k = \pm 1$, in
 which a value of 0.65 T was used). The GSA Hamiltonian
 in Eq. (1) cannot account for the position of the BPI minima
 across all the resonances in Fig. 3 nor the difference in
 angles at which the BPI minima appear between resona-
 nces $k = 0$ [i.e., $32.6^\circ + n \times 60^\circ$, Fig. 2(a)] and $|k| > 0$
 $[47^\circ + n \times 60^\circ$, Fig. 2(d)], with a relative shift of
 $\Delta\phi = 14.4^\circ$. As mentioned above, a similar shift is also
 observed between the $k = 0$ BPI minima and the angles
 of the compensating field maxima [$\sim 50^\circ + n \times 60^\circ$,
 Fig. 2(c)], which also eludes explanation from Eq. (1).
 Interestingly, a 15° rotation of the trigonal O_4^3 with respect
 to the hexagonal O_6^6 transverse anisotropy term in Eq. (1)
 about the z axis can accurately account for all the
 observations (using $B_4^3 = -2.86 \times 10^{-4}$ and $B_6^6 =$
 11.46×10^{-7} K), as shown in Fig. S6. Note that this
 rotation is equivalent to the inclusion of an imaginary
 O_4^{-3} term, as expected from the C_{3v} symmetry of the
 molecule, although it does not give information about
 its physical origin. A more natural approach, with real
 physical significance, is to employ a multispin interaction
 Hamiltonian which takes into account the constituent
 ions and the corresponding intramolecular interactions,
 as follows:

FIG. 3 (color online). QTM probability of resonances $|k| = 0-3$
 as a function of transverse field applied along the axes at $\phi =$
 $32.2^\circ (+180^\circ)$ for $k = 0$, and $\phi = 107^\circ (+180^\circ)$ for $|k| > 0$. Clear
 BPI minima are observed at $H_T = \pm 1.05$, ± 0.57 , ± 0.50 , and
 ± 0.35 T for resonances $k = 0, \pm 1, \pm 2$, and ± 3 , respectively,
 as marked by the corresponding arrows. The inset shows a zoom to
 -0.6 to $+0.6$ T transverse field of the $k = \pm 3$ data. Reversal of
 the longitudinal field produces the specular image with respect to
 reversal of the transverse field, as imposed by the time-reversal
 invariance of the spin-orbit interaction.

$$\hat{H}_{\text{MS}} = \sum_i \hat{s}_i \cdot \overset{\leftrightarrow}{R}_i \cdot \overset{\leftrightarrow}{d}_i \cdot \overset{\leftrightarrow}{R}_i \cdot \hat{s}_i + \sum_i g\mu_B \hat{s}_i \cdot \vec{B} + \sum_{i>j} \hat{s}_i \cdot \overset{\leftrightarrow}{J}_{i,j} \cdot \hat{s}_j, \quad (2)$$

where $\hat{s}_i$ is the spin operator of the i th ion, $\overset{\leftrightarrow}{d}_i$ is a diagonal 3×3 matrix with values e_i , $-e_i$, and d_i (representing the rhombic and axial anisotropy terms of the i th ion), and $\overset{\leftrightarrow}{J}_{i,j}$ is the exchange coupling tensor between each pair (i, j) of spins. This model not only permits consideration of the couplings between the spins of the constituent ions (therefore explaining the presence of excited spin multiplets and accounting for all the observed QTM steps; see Fig. S1 in the Supplemental Material [19]), but also allows for an arbitrary rotation of the single-ion SOC tensors, achieved by the matrix $\overset{\leftrightarrow}{R}_i$ and characterized by the Euler angles α_i , β_i , and γ_i , as illustrated in Fig. 4.

The angles α_i and γ_i are identical for all ions (i.e., become simply α and γ), while β_i are spaced by 120° , as imposed by the molecular symmetry. All angles are unambiguously determined by the particulars of the BPI behavior within the transverse field magnitude-angle phase space (demonstrating the importance of observing the BPI). Our simulations indicate that varying α has a strong effect on the magnitudes of transverse field at which the minima occur for resonances $k = 1, 2, 3$. This dependence is shown in Fig. 4(a) as obtained from diagonalization of Eq. (2) using the following parameters: $g_i = 2$, $d = -3.6$ K, $e = 0.62$ K, isotropic $J = 3.1$ K, $\beta_1 = 0^\circ$, $\beta_2 = 120^\circ$, and $\beta_3 = 240^\circ$. Note that $k = 0$ remains unaffected for small values of α , which is no surprise as this resonance is the only one allowed in the absence of any local ion tilts. The positions at which we experimentally observe the minima are indicated in Fig. 4(a), and coincide with predicted values for a tilt of $\alpha = 6^\circ$. The value of γ generates an angular phase shift ($\Delta\phi$) between the modulation of the BPI in $k = 0$ and the other resonances, as shown in Fig. 4(b). The experimentally observed value for this shift is $\Delta\phi_{\text{exp}} = 14.5^\circ$, which agrees with the calculated difference for an angle of $\gamma = 33^\circ$ ($\Delta\phi_{\text{th}} = 14.4^\circ$). This set of angles explains all the novel experimental findings provided in this Letter, producing the BPI patterns displayed in Figs. S4 and S6 [19], including the fitting of the compensating longitudinal field in Fig. 2(c) (see the Supplemental Material [19] for details of the fitting).

An important aspect which is experimentally observed for the first time in these results is the difference between the transverse field dependencies of the $k = 1$ and $k = 2$ resonance splittings, with $\Delta_{k=1}$ growing much more slowly than $\Delta_{k=2}$ with increasing transverse field (Fig. 3). This is crucial in understanding the appearance of one of the two forbidden resonances, as the sole contribution of small internal transverse fields (dipole or hyperfine fields) can

FIG. 4 (color online). (a) Transverse field positions of the BPI minima for resonances $k = 0-3$ as a function of the Euler angle α , which represents the tilt of the ion easy axis away from the overall molecular easy z axis. The arrows indicate the values observed experimentally (see Fig. 3), which coincide for an angle of $\alpha = 6^\circ$. (b) Calculated angular positions of the BPI minima in resonances $k = 0$ and $k = 2$ as a function of the rotation Euler angle γ . The observed angular shift of $\Delta\phi_{\text{exp}} = 14.5^\circ$ is theoretically matched with a value of $\gamma = 33^\circ$. The inset illustrates an arbitrary α - β - γ Euler rotation of the second-order SOC tensor of a single manganese ion. The vector from the center of the triangle formed by the three ions to the first ion is approximately equivalent to the $\phi = 0$ (within the $\pm 3^\circ$ uncertainty in the exact position of the crystal in our sensor), which is coincident with the $\beta_1 = 0$ axis.

unfreeze QTM in resonance $k = 2$, while much larger field values would be necessary to similarly affect resonance $k = 1$. Together with the effect of local disorder-induced distortions (as discussed in Ref. [15]), this result may explain why QTM is observed at all resonances in most SMMs regardless of the selection rules imposed by the SOC symmetry.

Finally, the precision in the association of the MS Hamiltonian terms with the observed phenomena allows determination of the single-ion anisotropy tensors in relation to the specifics of the chemical arrangement with an unprecedented degree of accuracy, as we show in Sec. 5

of the Supplemental Material [19]. The magnetization studies presented here show a clear correlation between the chemical structure and the form of the SOC anisotropy or energy landscape of the spin of a SMM, and represent a nearly full treatment of QTM phenomenon. By illustrating the potential for such high-resolution examinations of the molecular symmetry, we see a vast and rich frontier remaining to be explored by the pairing of molecular engineering and low temperature physics experiment.

J. H. A. and E. d. B. acknowledge support from the National Science Foundation (Grant No. DMR 0747587).
10 E. K. B. thanks EPSRC for funding.

-
- 11** *To whom correspondence should be addressed.
 delbarco@physics.ucf.edu
- [1] Sessoli R, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature (London)* **365**, 141 (1993).
- [2] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, *Phys. Rev. Lett.* **76**, 3830 (1996).
- 12** [3] L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, *Nature (London)* **383**, 145 (1996).
- [4] D. Loss, D. P. DiVincenzo, and G. Grinstein, *Phys. Rev. Lett.* **69**, 3232 (1992).
- [5] J. von Delft and C. L. Henley, *Phys. Rev. Lett.* **69**, 3236 (1992).
- [6] A. Garg, *Europhys. Lett.* **22**, 205 (1993).
- [7] W. Wernsdorfer and R. Sessoli, *Science* **284**, 133 (1999).

- [8] E. del Barco, A. D. Kent, E. M. Rumberger, D. N. Hendrickson, and G. Christou, *Phys. Rev. Lett.* **91**, 047203 (2003).
- [9] S. T. Adams, E. da Silva Neto, S. Datta, J. Ware, C. Lampropoulos, G. Christou, Y. Myasoedov, E. Zeldov, and J. Friedman, *Phys. Rev. Lett.* **110**, 087205 (2013).
- [10] C. M. Ramsey, E. del Barco, S. Hill, S. J. Shah, C. C. Beedle, and D. N. Hendrickson, *Nat. Phys.* **4**, 277 (2008).
- [11] H. M. Qudusi, J. Liu, S. Singh, K. J. Heroux, E. del Barco, S. Hill, and D. N. Hendrickson, *Phys. Rev. Lett.* **106**, 227201 (2011).
- [12] J. J. Henderson, C. Koo, P. Feng, E. del Barco, S. Hill, I. Tupitsyn, P. Stamp, and D. Hendrickson, *Phys. Rev. Lett.* **103**, 017202 (2009).
- [13] J. Liu, E. del Barco, and S. Hill, *Phys. Rev. B* **85**, 012406 (2012).
- [14] J. Liu, E. del Barco, and S. Hill, *Molecular Magnets: Physics and Applications*, edited by J. Bartolome, F. Luis, and J. F. Fernandez (Springer, New York, 2013).
- [15] L. Sorace, M.-E. Boulon, P. Totaro, A. Cornia, J. Fernandes-Souares, and R. Sessoli, *Phys. Rev. B* **88**, 104407 (2013).
- [16] R. Inglis, S. M. Taylor, L. F. Jones, G. S. Papaefstathiou, S. P. Perlepes, S. Datta, S. Hill, W. Wernsdorfer, and E. K. Brechin, *Dalton Trans.* 9157 (2009). **13**
- [17] P. L. Feng, C. Koo, J. J. Henderson, M. Nakano, S. Hill, E. del Barco, and D. N. Hendrickson, *Inorg. Chem.* **47**, 8610 (2008).
- [18] C. Zener, *Proc. R. Soc. A* **137**, 696 (1932).
- [19] See the Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.000.000000> for details. **14**